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LETTER TO THE EDITOR

The trapping model for positrons diffusing inside the grain of arbitrary shape

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Abstract. We present a general solution of the trapping model for positrons which diffuse inside a grain of arbitrary shape towards its surface. The consideration takes into account both the diffusion and transition regime. The explicit form relations for the mean positron lifetime and the positron lifetime spectrum were obtained. The theoretical relation for the mean positron lifetime was analysed thoroughly for a grain of ellipsoidal shape. We established that the shape of the grain influenced the positron annihilation characteristics.

Positron annihilation spectroscopy is a well-established technique for the detection and study of vacancy-like defects in the crystalline structure. This originates from the fact that the positrons can be trapped at them and their annihilation characteristics differ from those corresponding to delocalized positrons. However, it is difficult to understand the experimental results when positrons annihilate in inhomogeneous, fine grained or highly deformed samples. This arises from the fact that the experimental results are usually interpreted using the standard trapping model, where the trapping of positrons in solids is described by kinetic equations. This model was first introduced by Brandt [1] who tried to explain the second lifetime in positron lifetime spectra measured in alkali halides. The model succeeded in many cases but for an inhomogeneous medium, the time-dependent diffusion equation is needed. The inhomogeneity means that the distance between the positron traps is comparable to the so-called diffusion length of the positron, equal to $L_+ = \sqrt{D_+\tau_f}$, where D_+ is the positron diffusion coefficient and τ_f is the positron mean lifetime in the bulk material. The typical value of this parameter is close to 0.1 μm for various materials. The trapping of positrons is controlled by two processes: first the diffusion towards the trap, and second, the transition from the free to the localized state. If the trapping is limited by the first process we call it the diffusion-limited regime; for the second process, it is the transition-limited regime. Brand and Paulin [2] first considered the trapping model but only in the diffusion-limited regime. There is some experimental evidence that this approach is not adequate to describe real experimental data (see e.g. [3–5]). Nowadays, we also have the solution of the trapping model in the diffusion–transition regime but only for the grain which has a symmetric form: sphere [6, 7], layer or fibre [5]. This is not adequate when we wish to study the fine grained sample or to deduce the trapping parameters; in this case we need to know how the shape of a grain influences the positron characteristics.

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The aim of this letter is to follow the exact solution of the trapping model in the diffusion–transition regime with no assumption about grain shape. We will apply the general solution to the case of a grain with ellipsoidal shape and test how deviation from a spherical shape influences the mean positron lifetime.

In the model, which we will call the diffusion trapping model (DTM), we assume that positrons diffuse in a perfect grain in which they annihilate with the rate: $\lambda_f = 1/\tau_f$, where τ_f is the mean positron lifetime in a free state. The grain surface is a perfect sink for positrons in which they are localized and then annihilate with the rate $\lambda_b < \lambda_f$. This is the so-called Smoluchowski boundary condition. The transition rate from the free to the localized state is described by the α parameter, the value of which is equal to the width of the boundary times the trapping rate parameter defined in the standard trapping model [1]. The number of trapped positrons, denoted as n_b, is a function of time. This is the same for the local positron concentration within the grain, $C(\boldsymbol{r}, t)$. Both functions fulfill the following set of equations

$$\begin{cases} \dfrac{\partial}{\partial t} C(\boldsymbol{r}, t) = D_+ \nabla^2 C(\boldsymbol{r}, t) - \lambda_f C(\boldsymbol{r}, t) \\ \dfrac{\mathrm{d}}{\mathrm{d}t} n_b(t) = \alpha \oiint \mathrm{d}S\, C(\boldsymbol{r}, t) - \lambda_b n_b(t) \\ D_+ \oiint_\Sigma \mathrm{d}\boldsymbol{S} \cdot \nabla C(\boldsymbol{r}, t) + \alpha \oiint_\Sigma \mathrm{d}S\, C(\boldsymbol{r}, t) = 0 \end{cases} \tag{1}$$

where Σ is the grain surface. The first equation is a diffusion equation for positrons which can also annihilate within the grain. The second one is the rate equation for the trapped positrons, and the third exhibits the fact that only the positrons which pass through the surface are able to be localized there. This last equation is the boundary condition for the first two equations. Our aim is to find a general solution of the set of equations, and in particular to find the function describing the time dependence of the total number of positrons:

$$n(t) = n_b(t) + \oiiint_\Omega \mathrm{d}V\, C(\boldsymbol{r}, t) \tag{2}$$

where Ω is the space inside the grain. From this equation we can evaluate the positron annihilation characteristics, namely, the positron lifetime spectrum $-\mathrm{d}n(t)/\mathrm{d}t$ or the mean positron lifetime defined as follows

$$\overline{\tau} = \int_0^\infty \mathrm{d}t\, t \left(-\frac{\mathrm{d}n}{\mathrm{d}t}\right) \equiv \int_0^\infty \mathrm{d}t\, n(t). \tag{3}$$

For the grain which has a symmetrical shape, layer, fibre or sphere, the solution of the DTM can be expressed in an analytical form as was presented in [5–7]. However, now we try to find a general solution of the problem when the grain has no specified shape. The efficient method of solution of the set (1) is to use the Laplace transformation for all the equations

$$\begin{cases} -C_0(\boldsymbol{r}, 0) + s\tilde{C}(\boldsymbol{r}, s) = D_+ \nabla^2 \tilde{C}(\boldsymbol{r}, s) - \lambda_f \tilde{C}(\boldsymbol{r}, s) \\ s\tilde{n}_b(s) = \alpha \oiint_\Sigma \mathrm{d}S\, \tilde{C}(\boldsymbol{r}, s) - \lambda_b \tilde{n}_b(s) \\ D_+ \oiint_\Sigma \mathrm{d}\boldsymbol{S} \cdot \nabla \tilde{C}(\boldsymbol{r}, s) + \alpha \oiint_\Sigma \mathrm{d}S\, \tilde{C}(\boldsymbol{r}, s) = 0. \end{cases} \tag{4}$$

In our consideration of this we assume that at $t = 0$, the positrons are uniformly distributed within the grain:

$$C_0(\boldsymbol{r},\,0) = \begin{cases} \dfrac{1}{V_\Omega} & \text{for } \boldsymbol{r} \text{ inside the grain} \\ 0 & \text{for } \boldsymbol{r} \text{ outside the grain} \end{cases} \tag{5}$$

where V_Ω is the grain volume and there are no positrons trapped at the grain boundary, that means $n_b(0) = 0$. This assumption is well justified in the conventional experiments where positrons implanted into the sample have a continuous energy spectrum. After some algebra and the application of the Gauss theorem we can convert (4) into the following set

$$\begin{cases} \nabla^2\tilde{C}(\boldsymbol{r},\,s) - [\gamma(s)]^2\tilde{C}(\boldsymbol{r},\,s) = -\dfrac{C_0(\boldsymbol{r},\,0)}{D_+} \\ \tilde{n}_b(s) = \dfrac{\alpha}{(\lambda_b + s)} \oiint_\Sigma \mathrm{d}S\,\tilde{C}(\boldsymbol{r},\,s) \\ D_+ \oiiint_\Omega \mathrm{d}V\,\nabla^2\tilde{C}(\boldsymbol{r},\,s) + \alpha \oiint_\Sigma \mathrm{d}S\,\tilde{C}(\boldsymbol{r},\,s) = 0 \end{cases} \tag{6}$$

where $\gamma(s) = \sqrt{(s + \lambda_f)/D_+}$, let us note that $\gamma(0) = 1/L_+$.

We define a new function

$$\tilde{F}(\boldsymbol{r},\,s) = \big(\lambda_f + s\big)V_\Omega\tilde{C}(\boldsymbol{r},\,s) \tag{7}$$

which according to the first equation of (6) fulfills inside the grain the following equation

$$\nabla^2\tilde{F}(\boldsymbol{r},\,s) - \gamma^2\tilde{F}(\boldsymbol{r},\,s) = -\gamma^2 \tag{8}$$

where $\gamma \equiv \gamma(s)$. The Laplace transform of the function which describes the change of the total number of positrons one can deduce from (7)

$$\tilde{n}(s) = \tilde{n}_b(s) + \frac{1}{(\lambda_f + s)}\frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}(\boldsymbol{r},\,s) \tag{9}$$

and from (6)

$$\tilde{n}(s) = \frac{1}{\lambda_b + s}\left[1 - \frac{\lambda_f - \lambda_b}{\lambda_f + s}\frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}(\boldsymbol{r},\,s)\right]. \tag{10}$$

The mean positron lifetime is described by

$$\overline{\tau} = \tilde{n}(0) = \frac{1}{\lambda_b} - \left(\frac{1}{\lambda_b} - \frac{1}{\lambda_f}\right)\frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}(\boldsymbol{r},\,0) \tag{11}$$

or

$$\overline{\tau} = \frac{1}{\lambda_f} + \left(\frac{1}{\lambda_b} - \frac{1}{\lambda_f}\right)\left[1 - \frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}(\boldsymbol{r},\,0)\right]. \tag{12}$$

The positron lifetime spectrum after the inverse of the Laplace transform is expressed as

$$\begin{aligned} -\frac{\mathrm{d}n(t)}{\mathrm{d}t} = {} & \lambda_b\left[1 - \frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}\big(\boldsymbol{r},-\lambda_b\big)\right]\exp\big(-\lambda_b t\big) \\ & + \sum_{i=0} \operatorname*{res}_{s=-\lambda_i} \frac{\lambda_i}{\lambda_b + s}\left[1 - \frac{\lambda_f - \lambda_b}{\lambda_f + s}\frac{1}{V_\Omega} \oiiint_\Omega \mathrm{d}V\,\tilde{F}(\boldsymbol{r},\,s)\right]\exp\big(-\lambda_i t\big). \end{aligned} \tag{13}$$

We note that the number of lifetime components depends only on the number of poles of the expression in the second brackets and it can be an infinite number. The interesting feature

is that the intensity of the longest lifetime component associated with λ_b has a similar form to the expression in brackets for the mean lifetime component (12); the only difference is that in the first case $s = -\lambda_b$ and in the second $s = 0$. It shows that one can evaluate the intensity of the longest lifetime component in the DTM from the mean lifetime component replacing L_+ by $L_+/\sqrt{1-(\lambda_b/\lambda_f)}$. This is a general property of the DTM, which does not depend on the grain shape. It shows that the study of the mean lifetime is of the same value as the study of the lifetime components in the positron lifetime spectrum.

The quantity

$$1 - \frac{1}{V_\Omega} \iiint_\Omega \mathrm{d}V\, \tilde{F}(\boldsymbol{r},\, 0)$$

describes the probability of positron annihilation at the grain boundary, so one can also deduce the relation for the so-called S-parameter measured in the Doppler broadening of annihilation line spectroscopy. In the relation (12) we only have to replace $1/\lambda_f$ by the S-parameter associated with positron annihilation in the free state, and $1/\lambda_b$ by the S-parameter in the localized state.

In order to find an explicit form of relation for the positron mean lifetime or the positron lifetime spectrum we have to solve equation (8). From the theory of the differential equation we know that its solution must have the following form

$$\tilde{F}(\boldsymbol{r},\, s) = A(s)\tilde{f}(\boldsymbol{r},\, s) + \tilde{g}(\boldsymbol{r},\, s) \tag{14}$$

where

$$\nabla^2 \tilde{f}(\boldsymbol{r},\, s) - \gamma^2 \tilde{f}(\boldsymbol{r},\, s) = 0. \tag{15}$$

The function $A(s)$ we can evaluate from the third equation of set (6)

$$A(s) = -\frac{(\lambda_f + s) \iiint_\Omega \mathrm{d}V\, [\tilde{g}(\boldsymbol{r},\, s) - 1] + \alpha \oiint_\Sigma \mathrm{d}S\, \tilde{g}(\boldsymbol{r},\, s)}{(\lambda_f + s) \iiint_\Omega \mathrm{d}V\, \tilde{f}(\boldsymbol{r},\, s) + \alpha \oiint_\Sigma \mathrm{d}S\, \tilde{f}(\boldsymbol{r},\, s)}. \tag{16}$$

Finally, we need only the following relation which can be expressed by $\tilde{f}$ and $\tilde{g}$ functions:

$$1 - \frac{1}{V_\Omega} \iiint_\Omega \mathrm{d}V\, \tilde{F}(\boldsymbol{r},\, s) = \frac{1}{1 + ((\lambda_f + s)/\alpha)B(\gamma)} \left[1 - \left(1 - \frac{B(\gamma)}{D(\gamma)} \right) \frac{1}{V_\Omega} \iiint_\Omega \mathrm{d}V\, \tilde{g}(\boldsymbol{r},\, s) \right] \tag{17}$$

where

$$B(\gamma) = \frac{\iiint_\Omega \mathrm{d}V\, \tilde{f}(\boldsymbol{r},\, s)}{\oiint_\Sigma \mathrm{d}S\, \tilde{f}(\boldsymbol{r},\, s)} \tag{18}$$

and

$$D(\gamma) = \frac{\iiint_\Omega \mathrm{d}V\, \tilde{g}(\boldsymbol{r},\, s)}{\oiint_\Sigma \mathrm{d}S\, \tilde{g}(\boldsymbol{r},\, s)}. \tag{19}$$

Thus, to solve the DTM, the exact solution of equation (8) is required, from which we can construct the functions $B(\gamma)$ and $D(\gamma)$ presented above.

Having the $B(\gamma)$ function we can also evaluate the values of λ_i in the relation for the positron lifetime as follows

$$\lambda_i = \lambda_f\left(1 - \frac{\xi_i^2}{\gamma^2(0)}\right) \equiv \lambda_f\left(1 - \xi_i^2 L_+^2\right) \tag{20}$$

where ξ_i fulfills the transcendental equation

$$\xi_i B\left(\xi_i\right) + \frac{\alpha}{D_+} = 0. \tag{21}$$

The above relation is valid for the grain of arbitrary shape. We can see that the solution of the DTM is always possible in a numerical form. In the case of a grain which has a simple symmetric shape, the solution can be expressed in an analytical form, e.g., for spherical grains the functions $B(\gamma)$ and $D(\gamma)$ can be written in an analytical form

$$B(\gamma) = \frac{1}{\gamma}\frac{i_1(\gamma\, R)}{i_0(\gamma\, R)} \tag{22}$$

and

$$D(\gamma) \quad = \frac{1}{3}R \tag{23}$$

$$\tilde{g}(\boldsymbol{r},\, s) = 1 \tag{24}$$

where

$$i_0(z) = \frac{\sinh(z)}{z} \qquad i_1(z) = \frac{\cosh(z)}{z} - \frac{\sinh(z)}{z^2}$$

and R is the sphere radius.

The solution of equation (8) in spherical co-ordinates has the following form

$$\tilde{F}(\boldsymbol{r},\, s) = \sum_{l,m}\left[E_{l,m}(\gamma) j_l(i\,\gamma\, r) + \gamma^2 \oiint_{\Omega} \mathrm{d}V'\, G_l\left(r,\, r'\right) Y_{l,m}^*\left(\theta',\, \varphi'\right)\right] Y_{l,m}(\theta,\, \varphi) \tag{25}$$

where $G_l(r,\, r') = -\gamma j_l(i\gamma r_<) h_l^{(1)}(i\gamma r_>)$ is the Green function, $i = \sqrt{-1}$, j_l is the spherical Bessel function, $h_l^{(1)}$ is the Hankel function, $r_<$ is the lesser of $(r,\, r')$ and $r_>$ is the greater of $(r,\, r')$. $Y_{l,m}(\theta,\, \varphi)$ are the spherical harmonic functions. This can be rewritten in the simpler form

$$\tilde{F}(\boldsymbol{r},\, s) = \sum_{l,m}\left[A_{l,m}(\gamma) j_l(i\,\gamma\, r) + \gamma^2 b_{l,m} \int_0^{\infty} \mathrm{d}r'(r')^2 G_l\left(r,\, r'\right)\right] Y_{l,m}(\theta,\, \varphi) \tag{26}$$

where $b_{l,m} = \oiint_{\Omega} \mathrm{d}\theta\, \mathrm{d}\varphi\, Y_{l,m}^*(\theta,\, \varphi)$. If we express the function $\tilde{F}(\boldsymbol{r},\, s)$ in the following way

$$\tilde{F}(\boldsymbol{r},\, s) = \sum_{l,m}\left[A_{l,m}(\gamma)\tilde{f}_{l,m}(\boldsymbol{r},\, s) + \tilde{g}_{l,m}(\boldsymbol{r},\, s)\right] \tag{27}$$

then expression (17) in spherical co-ordinates has the form

$$1 - \frac{1}{V_\Omega}\oiint_{\Omega} \mathrm{d}V\, \tilde{F}(\boldsymbol{r},\, s) = 1 - \sum_{l,m}\frac{1}{1 + ((\lambda_f + s)/\alpha) B_{l,m}(\gamma)}\left[\left(1 - \frac{B_{l,m}(\gamma)}{D_{l,m}(\gamma)}\right)\right.$$
$$\left.\times \frac{1}{V_\Omega}\oiint_{\Omega} \mathrm{d}V\, \tilde{g}_{l,m}(\boldsymbol{r},\, s) + \frac{(\lambda_f + s)}{\alpha} B_{l,m}(\gamma) b_{l,m} \frac{1}{V_\Omega}\oiint_{\Omega} \mathrm{d}V\, Y_{l,m}(\theta,\, \varphi)\right] \tag{28}$$

where

$$B_{l,m}(\gamma) = \frac{\oiiint_{\Omega} \mathrm{d}V\ \tilde{f}_{l,m}(\boldsymbol{r},\ s)}{\oiint_{\Sigma} \mathrm{d}S\ \tilde{f}_{l,m}(\boldsymbol{r},\ s)} \tag{29}$$

$$D_{l,m}(\gamma) = \frac{\oiiint_{\Omega} \mathrm{d}V\ \tilde{g}_{l,m}(\boldsymbol{r},\ s)}{\oiint_{\Sigma} \mathrm{d}S\ \tilde{g}_{l,m}(\boldsymbol{r},\ s)}. \tag{30}$$

The relation presented above allows us to solve the DTM for the case when the grain has an arbitrary shape, but the advantage of this expression is that we can expand the solution in a series and, in some complex calculations, take only the first terms.

We will apply the results presented above to consideration of the DTM of positrons in the symmetrical grain which has an ellipsoidal shape. The relation will be solved numerically. We will test how the shape of the grain affects the mean positron lifetime. Let us denote that the long axis of the ellipsoid has length $2R\epsilon$ and the short axis $2R$ (figure 1(a)). In our calculations we only take contributions with $l = 0$, $m = 0$ in the series (28), and we

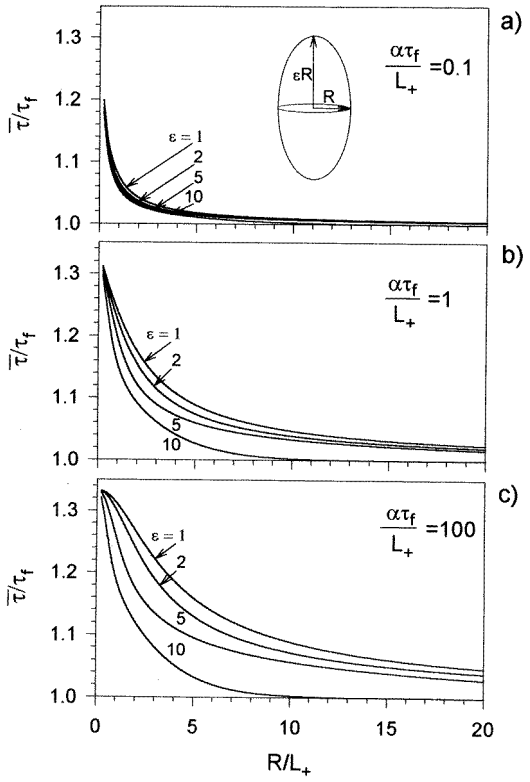

Figure 1. The mean positron lifetime, normalized to τ_f, versus R/L_+ calculated from the DTM for the ellipsoidal shape grain. The calculations were performed for three values of the $\alpha\tau_f/L_+$: (a) 0.1, (b) 1 and (c) 100 and four values of the ϵ parameter: 1, 2, 5 and 10 (note $\epsilon = 1$ corresponds to the spherical grain).

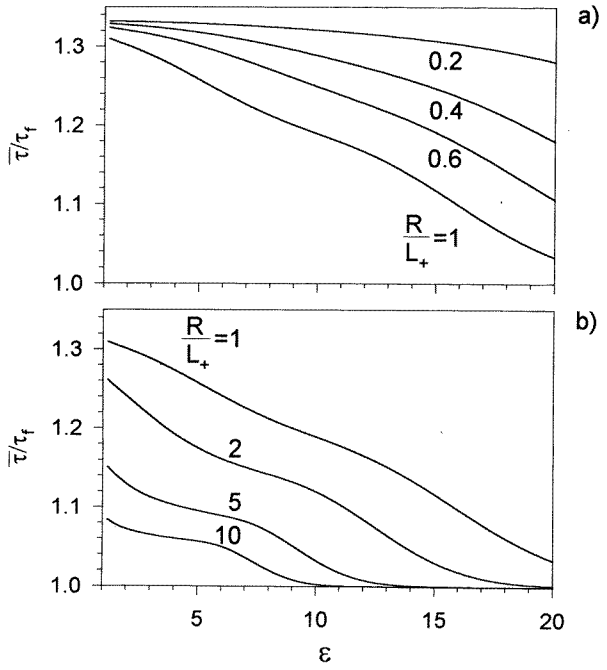

Figure 2. The mean positron lifetime, normalized to τ_f, versus the ϵ parameter, obtained in the frame of the DTM. The calculations were performed for several values of the R/L_+ parameter: (a) 0.2, 0.4, 0.6, 1 and (b) 1, 2, 5, 10. The parameter $\alpha\tau_f/L_+$ was equal to 100.

will consider the influence of the ϵ parameter only on the mean positron lifetime $\overline{\tau}$, see equation (12). Figure 1 presents the results of the numerical calculations of this quantity normalized to τ_f as the function of the ratio R/L_+, for different values of the parameter responsible for the transition positrons from free to the localized state $\alpha\tau_f/L_+$, and different ϵ parameter. The results for the spherical grain, the case of $\epsilon = 1$, we can take as a reference. First of all, we can see that the effect of the grain shape almost disappears when $\alpha\tau_f/L_+$ is small (figure 1(a)). It shows that when transitions from the free to the bound state of positrons limit the trapping process we can neglect the influence of the grain shape on the positron annihilation characteristics. But the shape is important when the diffusion is a slower process in comparison to the transition i.e. when $\alpha\tau_f/L_+$ is large (figures 1(b) and (c)). The increase of the ϵ parameter causes a faster decrease of the mean positron lifetime towards τ_f with the increase of R/L_+ in comparison to the spherical grain. We can easily understand this, as with the increase of ϵ more positrons will annihilate inside the grain and less will have a chance to arrive at the grain boundary. Nevertheless, this effect depends on the value of the ratio R/L_+, as we can see in figure 2. In this figure we looked at the effect of the ϵ parameter on the mean positron lifetime for various values of the R/L_+ parameter. We can see that if R/L_+ is less than 0.4 or higher than five the changes of the mean positron lifetime are less than 30%. We can thus conclude that the shape of the grain is an important feature which can effectively influence the positron annihilation characteristics. This makes it difficult to evaluate the real value of the diffusion and trapping parameters, L_+ and $\alpha\tau_f$, respectively. For example, if we had experimental data for the mean positron lifetime as a function of mean radius of the grains which have non-spherical shape, and we

tried to describe them using the formula for the sphere, the obtained L_+ parameter would then be overestimated in comparison to the real value. This effect seems to explain a small discrepancy between the value of the L_+ parameter obtained from the slow positron beam experiments and evaluated from the DTM, referred to in [8] and [5]. The authors believe that from positron annihilation characteristics, in the frame of the DTM, it is possible to deduce the shape of grains. It will be easier if we know, from other experiments, the L_+ and $\alpha\tau_f$ parameters.

In conclusion, the presented diffusion trapping model can solve the case of arbitrary shape grains. We have shown the general similarity between the relation for the mean positron lifetime and the relation on the intensity of the longest positron lifetime component deduced from the DTM. The numerical calculations performed for the grain of ellipsoidal shape have shown the significant influence of grain shape on the mean positron lifetime. This is valid only when the transition rate from free to the localized state at the boundary is high and the diffusion length of the positrons does not differ much from the size of grain.

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